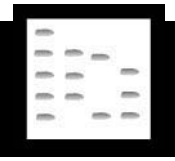
POLYCHLORINATED BIPHENYLS: GAS CHROMATOGRAPHY



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Introduction

From the initial detection of polychlorinated biphenyls (PCBs)* in biological tissue in the 1970s by Jensen there has been a continuous development in the analytical chromatographic techniques to determine these chemicals (**Table 1**). PCBs occur as complex mixtures which have a considerable impact on the cost of a complete analysis. Highly sophisticated techniques are required for the congener separation, and clean-up methods to prepare the samples tend to be labour intensive. Multi-residue methods in which several polyhalogenated hydrocarbons (PHHs) groups such as chlorobornanes (toxaphene), polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated diphenyl ethers (PCDEs) and their brominated homologues, can be determined in parallel are available, but this approach can lead to a compromise, resulting in lower recoveries and unresolved peaks in the chromatograms.

The first separation of PCBs was obtained using packed gas chromatographic columns with industrial formulations as calibration standards to quantify a single total value for the PCB. This early technology did not have the resolution to separate the PCBs into individual congeners and the most appropriate method to estimate these contaminants at that time was unquestionably by the summation of the peak heights or areas of the low resolution chromatogram. The continual development of sample preparation, chromatographic separation and the final determination has improved the reliability of the data in many laboratories. This has allowed a more detailed interpretation of the data, including the toxic non-ortho chloro and mono-ortho chlorobiphenyls (CBs).

Of the 209 CBs, 132 have been measured in industrial formulations at or above the 0.05% level. The original selection of CBs, made by the European Union Community Bureau of Reference in 1982, included CB 28, 52, 101, 118, 138, 153, and 180 and has now been adopted widely in many terrestrial, marine and food monitoring programmes. However this limited number of congeners was insufficient to study the specific toxicological effects and spatial patterns of these contaminants. These congeners, on their own, do not provide data for the TEQ† values needed for legislative or for environmental policy purposes.

The groups of toxic of CBs are:

Non-ortho CBs	CB 77, 81, 126, 169
Mono-ortho CBs (penta)	CB 105, 114, 118, 123
Mono-ortho CBs (hexa)	CB 156, 157, 167
Mono-ortho CBs (hepta)	CB 167

A schematic diagram of the isolation, separation, clean-up, group separation and final detection in environmental matrices in relation to the chromatographic separation of the congeners is given in **Figure 1**.

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Sample Preparation for Gas Chromatography (GC)

The main difficulties for CB analysis are still the separation of these congeners (i) from other co-extractants both at the bulk level, e.g. lipids, (ii) from other trace contaminants, e.g. chlorobornanes (toxaphene) and (iii) from other interfering congeners, e.g. CB 77 and CB 110. With the present methodology it is now possible to measure individual CBs routinely at the pg kg^{-1} and with care at the fg kg^{-1}. Trace amounts of co-extracted materials such as lipids, wax esters and sulfur degrade the analytical chromatographic column which is both expensive and time-consuming to replace. Effective clean-up of the sample extracts is essential prior to GC and liquid chromatography (LC)-GC separation because traces of lipids (0.1 mg) will become significant if the final sample volume is reduced to ca. 100 μL.

Destructive clean-up methods are mainly alkaline treatment (saponification) or oxidative dehydration (sulfuric acid treatment). Alkaline treatment is similar

*The term '*Polychlorinated Biphenyl* (*PCB*)' refers to the technical mixtures found in the formulation and the measurements made on the basis of calibration with these mixtures. *Chlorobiphenyl* (*CB*) refers to the individual congener named by the Ballschmiter number.

†TEQs refer to the sum of the concentration of the congener equivalent to 2, 3, 7, 8 TCDD obtained by using the toxic equivalence factor for each PCB.

Table 1 Chronological development of chlorobiphenyl analysis

Year	*Development*
1925	Large scale manufacture of PCB formulations.
1966	First reported measurement of PCBs as 'Avian Peaks'. Packed GC column separation of PCBs. Concentration in samples estimated against industrial formulations and summation of mixed component peaks in the chromatogram.
1969	Development of adsorption column chromatography for clean-up of biological tissue.
1975	Introduction of glass capillary columns. Improved separation of PCBs.
1970's	Development of stable GC evens and electronics to improve reproducibility of retention indices.
1980	Individual chlorobiphenyl congeners identified and systematically numbered. Introduction of fused silica capillary columns. Improved GC column stability.
1984	Retention times of all 209 CBs measured on an SE 54 capillary column.
1985	Reference materials, certified for individual CBs become available. Commercial availability of many of the 209 CBs. Reports of retention times on polar and semi-polar stationary phases. Development of multi-dimensional chromatography.
1988	Focus on the analysis of planar, toxic CBs and the application of toxic equivalence concentrations (TECs) for CBs as well as dioxins.
1989	Separation of CBs on the basis of their spatial configuration. Identification of all congeners present in main commercial formulations.
1989–1993	LC/GC coupled online. Development of multidimensional GC.
1990	Use of pyrenyl-silica HPLC for separation of non- and mono-ortho CBs.
1990's	Development and application of novel extraction techniques including accelerated solvent extraction, microwave assisted extraction, Soxhtec, supercritical fluid extraction.
1992	Expansion of retention data for 5 GC phases of different polarity for all congeners in commercial mixtures ($> 0.05\%$), except CB 69, 75, 96 and 182; series coupled columns.
1993	SFE-GC coupled techniques.
1995	Improvements of pyrenyl-silica HPLC separation through temperature control.
1994/8	Use of pyrenyl-silica column for separation of CBs and PCDD/Fs.
1997/9	Modular multidimensional gas chromatography.

to the saponification used in conjunction with extraction, but is applied sequentially to the solvent extraction instead of applying it to the matrix directly.

Non-destructive methods use solid-phase columns, gel permeation techniques and dialysis. Alumina columns are very effective and probably one of the most frequently used clean-up methods. Silica and florisil columns are alternative adsorbents. Gel Permeation Chromatography (GPC) or size exclusion chromatography (SEC) has also been used for lipid removal and for separation based on molecular size. SX-3 Bio Beads are used in most cases. Dialysis techniques include the use of a polythene film of pore size ca. 50 μm. The CBs migrate from the fat through the polythene tube to the cyclohexane solvent surrounding the tube. Dynamic dialysis inside a Soxhlet gives a recovery of over 95% in 8 h. The rate of dialysis is temperature dependent with the optimum temperature being around 43°C, above which the lipids are also dialysed at an unacceptable rate. Sulfur must be removed from the sample extracts by percolation through an activated copper column, since the element is sufficiently soluble in organic solvents and, in large quantities, can completely saturate the detector signal, particularly the ECD.

Group Separation

Group separation of the CBs is necessary (i) to separate the non-ortho CBs and the mono-ortho CBs that occur at relatively lower concentrations, e.g. CB 105, CB 156 from the other congeners, (ii) to remove other interfering PHHs and (iii) to remove further traces of co-extracted material remaining from the extraction of the bulk matrix.

Silica gel columns containing 1–2 g of adsorbent are frequently used to obtain such a pre-separation. The CBs and chlorobenzenes are eluted with a non-polar solvent (hexane or iso-octane) in the first fraction. Other sorbents such as florisil have also been used.

The isolation of the non-ortho CBs is based primarily on the planarity of the molecule compared with the ortho CBs, and as such these congeners tend to be separated along with other planar PHHs. There are three techniques used to fractionate PCDDs, PCDFs and planar CBs. These methods use gravity carbon columns, HPLC with graphitized carbon columns and HPLC with PYE [2-(1-pyrenyl) ethyl dimethyl silica] columns. Other HPLC column phases have been developed to isolate the planar contaminants from other PHHs including 2,4-dinitrophenyl mer-

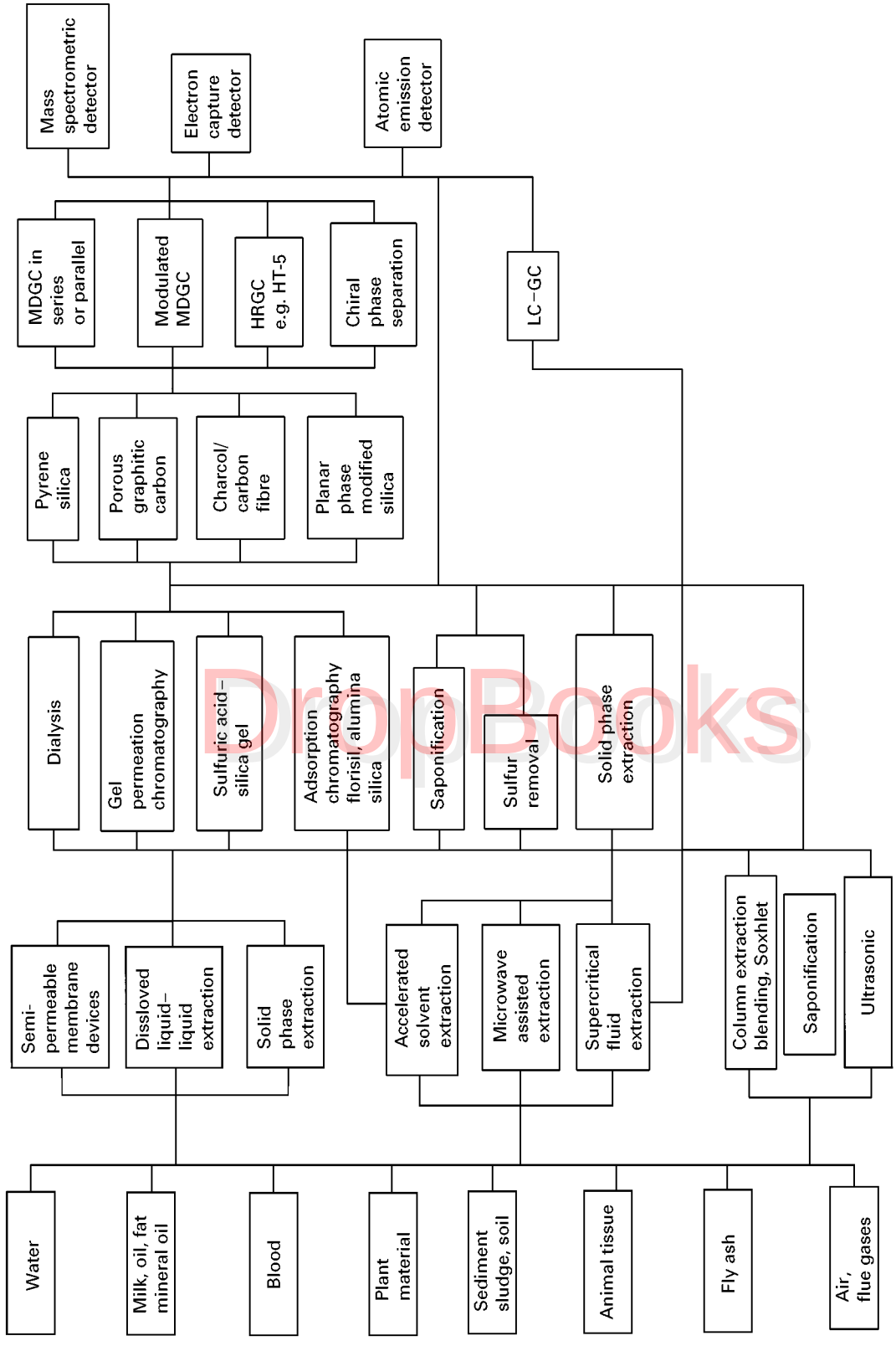

Figure 1 The schematic flow diagram of the analysis of chlorobiphenyls. The connecting routes show the types of environmental samples, the methods of extraction which are currently available, the clean-up techniques, the group separation, high resolution chromatographic separation and the range of detectors used for the final measurement.

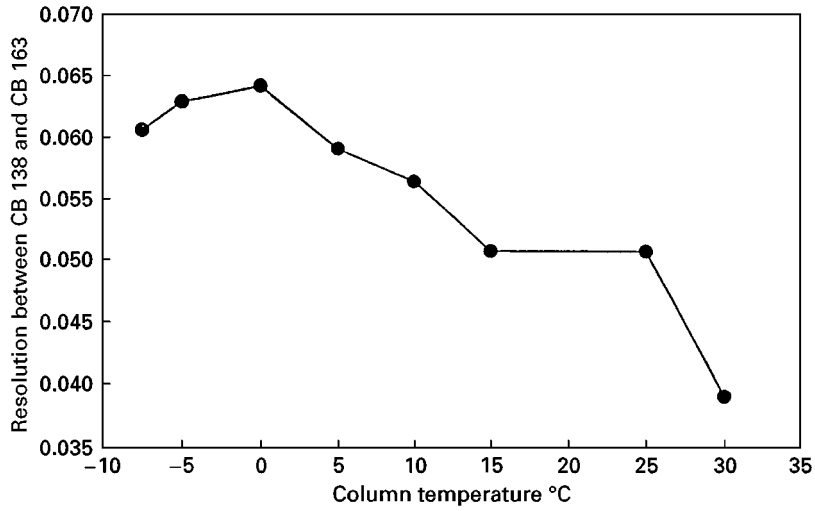

Figure 2 The resolution between CB 138 and CB 163 on a pyrenyl-silica HPLC column, 250 × 0.46 mm. i.d. as a function of the column temperature. The maximum resolution occurs around 0°C. The column cooling was controlled by a solid-state Peltier heat pump.

captopropyl silica (DNPMP), dinitroanalinepropyl silica (DNAP) and tetranitrofluoriniminopropyl silica (TENF). When the congeners are finally determined by GC, it is not necessary for them to be resolved from each other by HPLC.

The separation of CBs on the Comosil PYE column is temperature dependent (**Figure 2**). One of the more difficult separations between CB 138 and CB 163 on most GC columns* is possible on the PYE column providing that the column temperature is reduced to ca. 0°C. The porous graphitic carbon column to separate CB 77 and CB 110 along with the other non-ortho and mono-ortho CBs uses a double forward and reverse constant flow with hexane as an eluant.

LC-GC Combinations

Linking LC with GC aids the development of automated analysis and reduces the likelihood of contamination. There is also a substantial increase in the resolving power of 2D chromatography over a single system, especially where the polarity of the phases is orthogonal. The preferred combination of columns can sometimes be difficult because the polarity of the phases and the solvents used can make the linking difficult. Interfacing the LC to the GC has also been hampered by the relative volumes of the carrier fluids (liquids and gases). Rather than have a continuous flow-through system, we can overcome both difficulties in linking LC with GC by using the modulated approach by cryofocusing the eluate from the first column, removing the first solvent before flushing onto the second column with an alternative fluid, i.e. a second solvent in the case of LC-LC, or by flash vaporizing into the carrier gas in the case of LC-GC.

Gas Chromatography

The chromatographic separation techniques for different congener groups is given in **Table 2**.

Sample Injection

There are three main injection techniques used in the analysis of CBs in environmental tissues, the splitless, the programmed temperature vaporizing (PTV), and the on-column injector. The splitless injector is used by most laboratories for CB analysis and must be optimized for splitter time, needle length in relation to the length and volume of the injector, and the type and cleanliness of the injection liner. The advantage of the on-column over the splitless injector is that the optimum conditions are more straightforward and there is less opportunity for mass discrimination over the range of CBs, primarily since all of the sample is injected onto the column. However, the sample must undergo a rigorous clean-up. Insufficiently cleaned samples seriously affect the column performance when using an on-column injector, whereas analyses with a splitless injector are less affected by non-volatile deposits. Only the glass liner requires regular, routine replacement.

Chromatographic Phases

Packed columns used in the 1970s and early 1980s have been replaced initially by glass and then by higher resolution, polyimide coated, fused silica cap-

*The separation between CB 138 and CB 163 can now be achieved using the HT5 stationary phase.

Table 2 Chromatographic separation techniques for different groups of congeners

Congener	*Group*		
	Major mono-ortho CBs 105, 118, 156	*Minor mono-ortho CBs 114, 123, 157, 167, 189*	*Non-ortho CBs 77, 126, 169*
Single techniques			
Single-column GC without pre-separation	Possible with care	Difficult	Currently not possible
LC (with diode-array)	Currently not possible	Currently not possible	Possible with care at relatively high levels
MDGC	Easy	Easy	Difficult
Hyphenated techniques			
LC-GC online	Difficult	Difficult	Difficult
Adsorption charcoal	Easy	Difficult	Difficult
PGC*-HPLC-GC offline	Easy	Easy	Easy
PYE-HPLC-GC offline			
LC-GC offine	Easy	Easy	Easy

* PGC, porous graphitic carbon.

illary columns. Stationary phases of different polarities can be used for the determination of CBs, but non-polar and medium-polar phases generally offer a higher resolution.

A number of stationary phases tailored to the separation of CBs (**Table 3**) have shown considerable improvement over the more conventional proprietary phases available. These phases have had greater success in separating additional congeners when used in series with more conventional columns. A 1,2-dicarba-*closo*-dodecacarborane polydimethylsiloxane (HT-5) column has been used in series with a CPSil-8 (5% diphenyl polydimethylsiloxane) column with helium as carrier gas to separate 84 congeners using an electron-capture detector (ECD) (and 108 congeners using mass spectrometry detection (MS)). The HT-5 column has an upper temperature limit in excess of 300°C enabling fast temperature programming and analysis in less than 60 min. The HT-5 phase has been further optimized by using a 60 m × 0.25 μm i.d. fused silica column with a film thickness of 0.25 μm able to separate 106 congeners with ECD and 138 congeners with MS. This includes the separation of the critical CB 138/CB 163 pair. A prototype smectic liquid-crystalline polysiloxane column is able to separate some CB mixtures that have been more difficult to separate on more conventional columns such as CB 28/31 and CB 138/163. This phase is also useful to separate the non-ortho and mono-ortho CBs.

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Table 3 Co-elution CBS on capillary GC columns with different stationary phases

Congener	*HT-5*	*CPSil 5*	*CPSil 8*	*CPSil 19*	*CPSil 88*	*CPSil 8/HT-5*
28	–	–	–	–	16	–
52	–	–	–	–	–	–
77	149	–	110	–	82/183/187	–
101	60	–	84	–	55	84
105	141	132	132	–	129	–
118	–	–	149	–	200/123	149
126	167/185/202	129	129/178	–	–	–
128	159/174	–	167	–	193/201	167
138	–	160/163	160/163	160/163/158	–	160/163
153	–	–	–	–	–	–
156	172	171	202/171	–	–	202
157	–	202	173/200	180/197	–	–
158	175/178	–	–	163/138	138/160	–
169	–	–	–	203/196	–	–
170	–	–	190	190	–	–
180	193	–	–	197	197	–
194	–	–	–	–	–	–

Multidimensional Gas Chromatography (MDGC)

Currently, all of the ca. 132 congeners detectable in formulations and environmental matrices cannot be separated on a single GC or HPLC column (Table 2). However, the separation power can be substantially increased when columns are coupled either in series or in parallel. The greatest separation is obtained by using different systems and/or phase types to maximize the orthogonality of the separations. Multiple columns such as serially-coupled columns parallel-coupled columns, two-dimensional GC and, recently, comprehensive multidimensional GC (MDGC) have been developed to provide greater resolution of complex mixtures such as CBs.

In two-dimensional GC co-eluting compounds are 'heart-cuts' as they elute from the first capillary column and are transferred to a second capillary column of a different polarity which is able to separate the isolated group of compounds. This technique offers a complete separation of certain groups of unresolved congeners which are 'heart-cut' from the first column. The technique is limited by the number of 'heart-cuts' which can be made in one chromatographic run, since more than three to four lead to peak overlap on the second column. Analysis times of the 'heart-cut' two-dimensional GC are also relatively long. Nevertheless this technique has been applied to the determination of CBs in environmental samples. The mono-ortho CBs 60, 74, 114, 123, 157, 167 and 189 have been determined in Aroclor mixtures and seal tissue using MDGC with ECD combining the Ultra 2 and FFAP columns. This direct method was found to be preferable to the separation of the mono-ortho CBs and the other congeners by HPLC. Either MDGC or off line HPLC separation of the mono-ortho CBs is often necessary to reduce the risk of false positive results from interferences since these congeners occur at relatively lower concentrations compared with the di- and tri-ortho CBs.

Comprehensive, modulation MDGC yields truly three-dimensional chromatograms (2D time base $\times$ concentration). Two capillary columns are connected in series by a retention gap which can be heated very quickly in a reproducible way. The eluants from the first column are cryofocused in the retention gap for a period of ca. 3 min, after which time the retention gap, which has a minimum thermal capacity, is heated quickly to 'inject' the focussed compounds onto the second column of different polarity. The second chromatogram lasts for approximately the same period of time as the period of cryofocusing, so that a time series of 3 min chromatograms are produced to provide a two-dimensional separation (**Figure 3**). Because peaks collected at the modulator are very highly focussed before they enter the second column, an extremely high sensitivity can be obtained in combination with a very high selectivity.

Chiral Separation

Of the 209 CBs, 78 display axial chirality due to the steric hindrance to free rotation about the C–C axis of the two aryl rings, and of these 19 possess 3 or 4 chlorine atoms in the ortho position. The CBs 84, 88, 91, **95**, 131, **132**, 136, **149**, 171, **174**, 183, and 196 are present in commercial mixtures; the four in bold type are present above the 2% level. GC separation of the 19 stable atropisomers have been made on the following columns:

2,3,6-Tri-O-methyl-β-cyclodextrin
2,3-Di-O-methyl-6-O-hexyldimethylsilyl-β-cyclodextrin
2-6-Di-methyl-3-O-n-pentyl-γ-cyclodextrin
6-O-tert-Butyldimethylsilyl-2,3-di-O-methyl-β-cyclodextrin
tert-Butyldimethlysilylated-β-cyclodextrin.

The enantiopure CBs have been isolated by chiral HPLC. The (−) CBs 84, 132, 136, and 176 eluted befor the (+) enantiomers while the order was reverse for CB 135 and 175. The enantiomers CB 95, CB 132 and CB 149 in Clophen A60 have been separated using MDGC to 'heart-cut' the congeners from the first column (DB-5) onto the second chiral phase, heptakis (2,3,6-tri-O-methyl)-β-cyclodextrin (Chirasil-Dex). However, to date none of the enantiomers have been shown to be specifically toxic or able to induce any observable biological effect.

Detection

The power of the GC separation, especially with the thin (0.1 μm) film phases, must be matched by the sensitivity and the specificity of the detector to measure concentrations of CBs at the 10^{-12}–10^{-14} level. These low levels of detection are required for the analysis of samples from relatively clean areas of the environment, for example the polar regions, oceanic and remote atmospheric samples. They are also required for samples obtained from small organs from single animals taken as part of biological effects studies or the investigative analysis of human adipose tissue.

Insufficient chromatographic resolution and incorrect calibration of the detector (Table 3) are still the primary source of error in the determination of CBs by GC. Errors associated with the calibration of the detector can be greatly reduced by implementing the

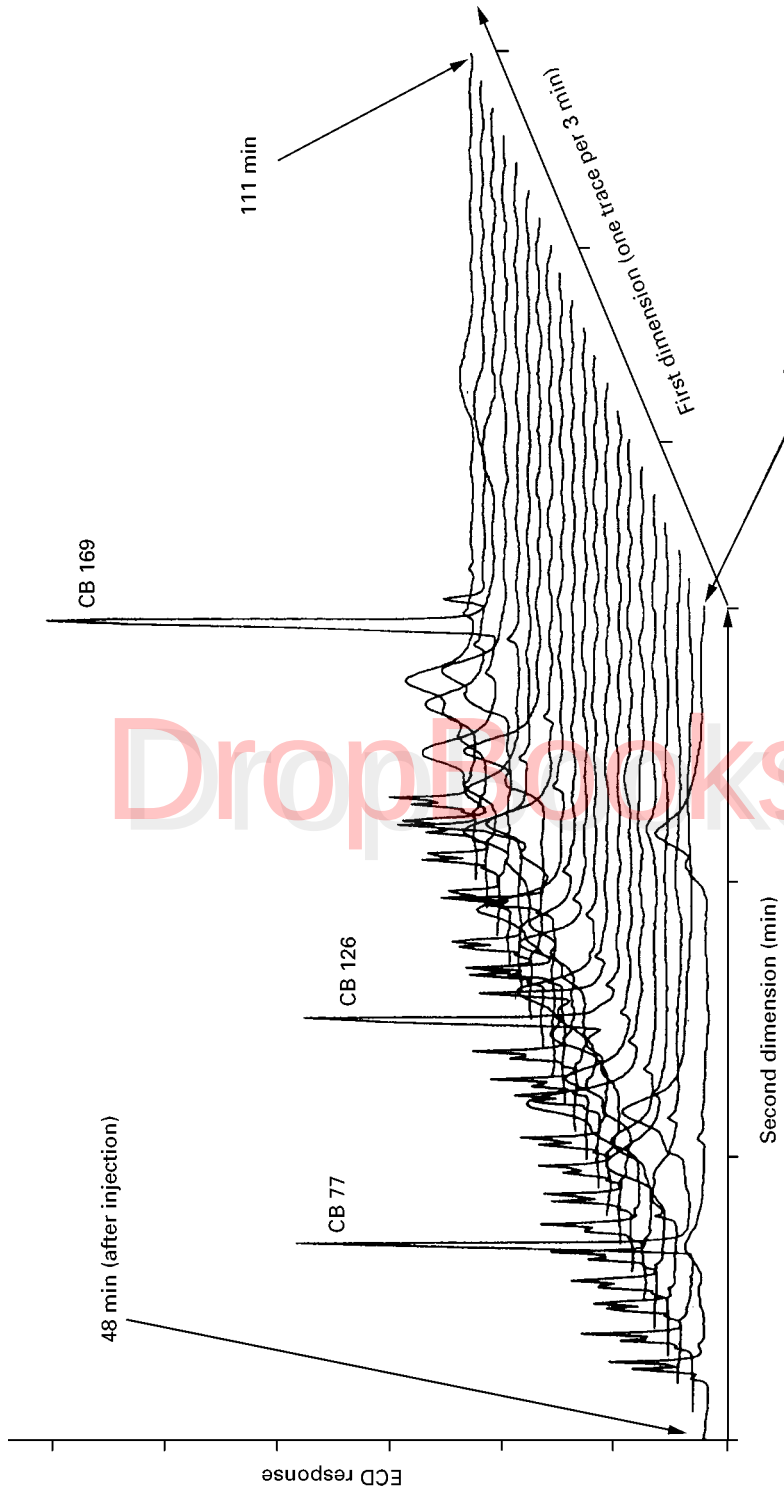

Figure 3 GC-ECD chromatogram of CB 77, CB 126, CB 169 showing the use of the Thermal Desorption Modulator (TDM). The first column was 24 m × 0.2 mm i.d. 0.15 µm SB smectic phase, 24 cm 0.1 mm i.d. 0.12 µm CP Sil 8 TDM and a 5.3 × 0.2 mm i.d. 0.33 µm Ultra 2 second column. The TDM wad desorbed every 3 min. (Reproduced from Geus H-J de, Boer J de and Brinkman UA (1997) *J. Chromatogr.* 767: 137–151, with permission, from Elsevier Science.)

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following guidelines:

- only use certified solids or solutions. These are available for most congeners;
- confirm the identity of the material(s) provided by MS;
- contol the preparation dilution and storage of calibrants by weight;
- store ampoule stock and working calibration solutions in a cool dark place. Avoid using screw top containers and do not store screw top containers in the refrigerator;
- confirm the purity of all solvents used by concentrating to ca. $\times 100$ and analysing with an ECD and an FID;
- calibrate the detector with sufficient frequency to ensure the response factor for each congener is ca. $< \pm 5\%$ of the actual response;
- check the frequency of calibration, which is a function of the cleanliness of the GC system;
- check new stock solutions against previous calibration solutions or against independent solutions of known quality.

A summary of the detectors which have been used for the determination of CBs is given in **Tables 4** and **5** along with the relative advantages, disadvantages, relative cost and current detection limits. ECDs were used initially because of their high sensitivity for electronegative compounds, but MS detection has become a routine method for measurement. Modern MS instruments are easy to operate, are more selective than the ECD, and have a better linear range.

Electron-Capture Detection

The most widely used detector for CB analysis is still the ECD. It is inexpensive, easy to use, highly sensitive and selective towards halogenated compounds containing one or more halogen atoms. Unfortunately the detector is not only sensitive to the number of halogen atoms, but also to the spatial configuration of the molecules and its cross sectional area. This means that the detector response is specific not only to each congener, but also to its enantiomers, if they exist. The detector also has a small linear range, making it effectively non-linear requiring both constant and multi-level calibration, although the small (380 μL) frequency pulsed, constant current detectors have extended the linear range. Recently a micro-ECD with a cell size of ca. 150 μL has been developed to further improve sensitivity and linear dynamic range.

Mass Spectrometry

The mass spectrometric detector (MSD) is fast becoming the preferred alternative to the ECD. The simpler MSD and Ion Trap Detectors (ITDs) have been fully integrated with capillary GC and most instruments now have a fused silica column terminating inside the ion source of the MS. The ITD differs from other MS techniques in that the ions formed by ionisation are trapped electronically and then destabilized according to their mass and transferred to the electron multiplier outside the trap itself. The MSD is now a robust instrument and although it requires more specialist attention than the ECD, it does offer considerably more power in terms of sensitivity, selectivity and confirmatory analysis. The MSD has a much wider linear range than the conventional ECD used for much of the routine CB analysis.

The high resolution MS provides highly specific mass detection with resolution between 6000 and 10 000 provided by accurate mass marking with PFK at m/e 316.9824 to prevent mass drift. This not only offers a high specificity, but also considerably reduces the likely interference with other trace contaminants such as PCDDs and PCDFs.

A further advantage of MS is provided by the increased sensitivity of Negative Ion Chemical Ionization (NICI) with molecules containing more than four chlorine atoms. The sensitivity can be further

Table 4 Summary of methods of calibration

Type	*Use/advantage*	*Misuse/disadvantage*
Single point calibration	Semi-quantitative, screening technique, calibrant and sample within ca $\pm$ 5–10% linear detectors	Inaccurate, especially at low concentrations. Not suited to the ECD
Bracketing standards	Small linear range of the ECD. MS detection	Extrapolation beyond the upper and lower limits
Multipoint calibration	Most accurate method for ECD. Requires quadratic or cubic spline type curve fit	Time-consuming in use, maintenance of calibration solutions
Labelled internal standards ^{13}C, ^{2}H	Mass spectrometric detector, compensates for all recovery losses	Not suitable for ECD. Does not give any information on the intrinsic efficiency of the method.

Table 5 Detectors used for the determination of CBs by gas chromatography

Detector	*Advantages*	*Disadvantages*	*Detection level*	*Relative cost*
High resolution MS (HRMS)	Very high specificity and sensitivity. Provides spectral identification. Use ^{13}C labelled analogues	Highly specialized operation High capital and maintenance cost	Low ng kg^{-1}	Very high*****
Isotope dilution MS (IDMS)	Very high specificity and sensitivity. Provides spectral identification. Use ^{13}C labelled analogues	Highly specialized operation High capital and maintenance cost	5 ρg kg^{-1}	Very high**
Low resolution (LRMS) quadrupole and MSD	Used primarily as an GC detector	Specialist operation Moderate capital and maintenance cost	CB 28 PCl 200 μg kg^{-1} NCl 700 μg kg^{-1} CB 80 PCl 253 μg kg^{-1} NCl 2.2 μg kg^{-1}	High*****
Ion trap detector (ITD)	Used primarily as a GC detector	Specialist operation Low maintenance cost Own ITD MS library	Low μg kg^{-1}	Moderate*****
MS-MS	Separation of unresolved compounds in the MS itself	Specialist operation High capital and maintenace cost	Low ng kg^{-1}	Very high*****
Flame ionization detector (FID)	Simple and easy to use. Good linearity. Useful as a check on clean-up efficiency	Poor sensitivity and specificity.	0.5 mg kg^{-1}	Low*
Atomic emission detector (AED)	Response only dependent on elemental composition Robust and stable	Poor sensitivity	0.1 mg kg^{-1}	Moderate***
Electron-capture detector (ECD)	Very sensitive. Inexpensive. Directly coupled to GC	Only selective for electron capturing material like halogenated hydro-carbons Response dependent on molecular structure. Small linear range	0.1 μg kg^{-1}	Low*****

***** Very applicable.
* Not very applicable.

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enhanced by operating in the selective ion monitoring (SIM) or multiple ion monitoring (MIM) modes as opposed to the total (full scan) ion current mode (TIC). The main disadvantage with using the MS in SIM or MIM is that the confirmatory power of the technique is considerably reduced. In this mode the CBs generate a strong molecular base peak with a limit of detection (LOD) of 40–100 fg. One of the main advantages of MS, in addition to sensitivity and specificity, is the ability to use ^{13}C labelled compounds as internal standards to compensate for losses during sample preparation, especially at the fg level. Using ^{13}C congeners reduces the need for extensive recovery experiments or having to apply recovery corrections in the method validation and improves the overall variance of the data. High resolution capillary GC coupled with tandem MS-MS provide a very powerful separation technique both by the chromatography but also in the mass spectrometer itself. The MS-MS will separate components that are not resolved by a single GC-MS alone.

Atomic Emission Detector (AED)

The AED is a well established and widely used detector for elemental analysis. Although the AED has an excellent sensitivity for most elements, it has a low relative sensitivity for halogens. As a result it has tended to be overlooked as a detector for trace organic contaminants in favour of the ECD and more recently the MSD. The AED is relatively very stable and, in contrast to the ECD, has a common molar response for compounds of equal halogen content.

Commercial AED instrumentation, with a detection limit of ca. 250–400 pg, has been too insensitive for the determination of CBs in all but the most contaminated samples. Recent AED development has used a 350 kHz on-column RF plasma set at 837.6 nm for the CI emission operating at 350°C with He at 10 mL min^{-1} as make-up gas and O_2 as the plasma dopant. The capillary column is positioned so as to sustain the plasma *inside* the end of the column. This 'on-column' configuration improves the detection limit by $\times 30$ and provides sufficient sensitivity to be compared directly with the ECD in the analysis of real sediment samples.

See also: **II/Chromatography: Gas:** Detectors: Mass Spectrometry; Detectors: Selective; Multidimensional Gas Chromatography; Sampling Systems; **Extraction:** Solid-Phase Extraction. **III/Insecticides:** Gas Chromatography; **Pesticides:** Gas Chromatography.

Further Reading

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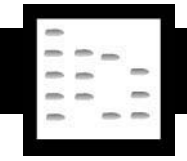
POLYCYCLIC AROMATIC HYDROCARBONS



Gas Chromatography

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Introduction

Polyaromatic hydrocarbons (PAHs) constitute a very extensive and probably the most structurally assorted group of organic compounds. They are ubiquitous to the environment, and may well be the most widely studied class of environmental pollutants. Unfortunately, because of their diverse nature, there is no single nomenclature that describes collectively these compounds to everyone's satisfaction. Thus, one is likely to come across the terms polyaromatic hydrocarbons, polyaromatic compounds, polynuclear aromatic hydrocarbons or polycyclic aromatic hydrocarbons in the scientific literature, even though all may actually be referring to this same class of chemicals. For the purpose of this article, PAH is used in the broadest sense possible, so that even those compounds that contain atoms other than carbon and hydrogen may be included in the discussion.

PAHs are formed primarily from the combustion of fossil fuels, with major sources being of anthropogenic origin, although bacteria and plants also contribute some PAHs to the environment. Interest in these compounds dates back to 18th-century England when it was suggested that scrotal cancer afflicting chimney sweeps could have been caused by substances present in soot from burning coal. PAHs were still unknown at that time, of course. It was only 150 years later, in the 1930s, that it was finally confirmed that soot contains benzo[*a*]pyrene and dibenz[*a*,*h*]anthracene, two PAHs with carcinogenic properties. Research into PAHs was given significant impetus by this discovery and, to this day, enormous interest is still focused on these compounds, not only in studies